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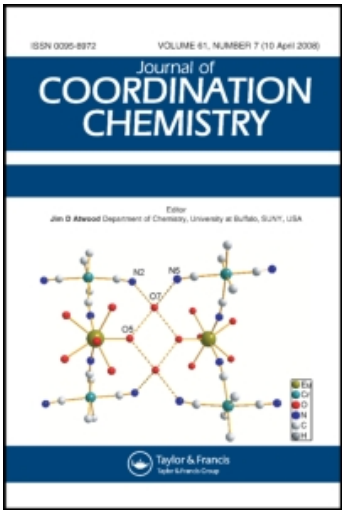

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Chemical, spectroscopic characterization, and *in vitro* antibacterial studies of a new gold(I) complex with *N*-acetyl-L-cysteine

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Chemical, spectroscopic characterization, and *in vitro* antibacterial studies of a new gold(I) complex with *N*-acetyl-L-cysteine

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A new gold(I) complex with *N*-acetyl-L-cysteine was synthesized and characterized by chemical and spectroscopic techniques. The elemental and thermal analyses of the solid compound fit to the composition $AuC_5H_8NO_3S \cdot 0.75H_2O$. Solid-state ^{13}C-nuclear magnetic resonance (SSNMR) and infrared (IR) analyses indicate the coordination of the ligand to Au(I) through sulfur. The insolubility of the complex in both polar and non-polar solvents supports a polymeric structure. The antibacterial activity of the complex was evaluated by antibiogram assays using the disc diffusion method. The compound showed effective antibacterial activity against *Staphylococcus aureus* (Gram positive) and *Escherichia coli* (Gram negative) bacterial cells.

Keywords: Gold(I); *N*-acetyl-L-cysteine; Infrared spectroscopy; NMR spectroscopy; Antibacterial activity

1. Introduction

Gold compounds have been used in pharmacology and medicine for the treatment of different human malignancies. Myochrysine and solganol, which are thiolate-supported gold(I) compounds, are two of the best examples of chemotherapeutic applications of gold complexes with bioactive ligands in modern medicine. Both compounds have been extensively used for the treatment of rheumatoid arthritis [1, 2]. Auranofin, a phosphine-supported gold(I) complex, is another compound which has also been used for the treatment of rheumatoid arthritis. The mechanism of action of auranofin seems to be closely related to the suppression of COX-2, a pro-inflammatory enzyme [3]. A great deal of attention has been paid to the close relationships between metals, or

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their complexes, and carcinogenesis. The treatment of a variety of cancers by cisplatin (*cis*-diamminedichloridoplatinum(II) [$PtCl_2(NH_3)_2$]) has stimulated on-going investigations on alternative metal-based drugs such as auranofin, and their uses in anticancer therapy [4–7]. Recently, the new gold(I) complex chlorotriphenylphosphine-1,3-bis(diphenylphosphino)propanegold(I) showed promising *in vitro* antitumor activity in the initial protocols against human tumors [8]. Also, the *in vitro* antitumor hepatotoxicity of bidentate phenyl and pyridyl complexes of Au(I) and Ag(I) have been described in the literature. Such compounds demonstrate the activity against cisplatin-resistant human cancer cells [9].

Gold(I) compounds have also been studied as antibacterial agents. Gold(I) complexes with N-donor heterocyclic ligands and triphenylphosphine [$Au(L)(PPh_3)$] (L = pyrazole or imidazole) exhibited selective antibiotic activity against *Bacillus subtilis* and *Staphylococcus aureus*, which are Gram-positive microorganisms [10]. Recently, the synthesis, characterization, and antimicrobial activities of new gold(I) analogs of the platinum complex with acridine (S-, N-donor ligand) were described; the gold(I) compounds exhibited pronounced and selective activity against *Mycobacterium tuberculosis* [11]. These data further support the promising approach of gold(I) in the field of tuberculosis treatment as it was already described for other gold(I) compounds [12]. In addition, the synthesis, characterization, and antibacterial activity against *Streptococcus pneumoniae* of gold(III) complexes with dithiocarbamates derived from amino acids (DL-alanine, DL-valine, and DL-leucine) were also described [13].

N-acetyl-L-cysteine ($C_5H_9NO_3S$, NAC) is a sulfur-containing amino acid present in vegetables and fruits such as asparagus, red pepper, lemons, and tomatoes [14]. The biological activities of NAC were recently described [15–18]. The synthesis, characterization, and reactivity of a dinuclear platinum(II) complex with NAC and bipyridine were also described, where NAC is coordinated to Pt(II) through sulfur and bridges the two metal centers [19]. More recently, new palladium(II) and platinum(II) complexes with NAC, in the anionic form, were synthesized in our laboratories [20, 21]. This article describes the synthesis, spectroscopic characterization, and biological studies of a new gold(I) complex with NAC.

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2. Experimental

2.1. *Reagents and equipment*

NAC (98%) and potassium dicyanoaurate(I) were purchased from Acros Organics and Sigma–Aldrich Laboratories, respectively. Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were performed using a CHNS-O EA1108 Analyzer, CE Instruments. Infrared (IR) spectra were measured using an Impact 400 Nicolet FT-IR spectrophotometer (FT, Fourier transform); The samples were prepared as KBr pellets. Solid-state ^{13}C-nuclear magnetic resonance (SSNMR) spectra were recorded on a Varian INOVA 300 MHz spectrometer equipped with a MAS 7-mm probe. The CP/MAS spectra were measured at a spin rate of 4.5 kHz and rf pulse of $\pi/2$. The contact time was 2.0 ms and the recycle delay time was 7 s. The ^{13}C-NMR–MAS spectra were acquired at 75 MHz. The samples were analyzed at room temperature and the chemical shifts were referenced to TMS. Thermal analyses were performed on a

Thermoanalyzer TGA/DTA-simultaneous SEIKO EXTAR 6000 in the following conditions: synthetic air, flux rate of $50\,cm^3\,min^{-1}$ and heating rate of $10^{\circ}C\,min^{-1}$, from 20°C to 900°C.

2.2. *Synthesis of the complex*

The gold(I) complex with NAC was synthesized by the reaction of 5.0 mL of an aqueous solution of potassium dicyanoaurate(I)–$K[Au(CN)_2]$ (1.0×10^{-3} mol) with 5.0 mL of a freshly prepared aqueous solution of NAC hydrochloride, containing 2.0×10^{-3} mol of the ligand. The synthesis of the complex was carried out with stirring at room temperature. After 1 h of constant stirring, the white solid obtained was collected by filtration, washed with cold water, and dried in a desiccator over P_4O_{10}. Anal. Calcd for $AuC_5H_8NO_3S \cdot 0.75H_2O$ (%): C, 16.1; H, 2.57; N, 3.76; S, 8.60. Found (%): C, 16.1; H, 2.79; N, 4.19; S, 8.74. Yield 45%. No single crystals were obtained, even after several attempts using a mixture of solvents (dimethylsulfoxide (DMSO): water in different proportions), in order to perform an X-ray structure characterization. The Au(I)–NAC complex is insoluble in water, ethanol, methanol, acetonitrile, chloroform, acetone, and hexane, and is slightly soluble in DMSO.

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2.3. *Biological assays*

Three referenced bacteria (*Escherichia coli* – ATCC 25922, *Pseudomonas aeruginosa* – ATCC 27853, and *S. aureus* – ATCC 25923) were used in this study. Antibiogram assay was performed by the disc diffusion method [22, 23]. The sensitivity of Au(I)–NAC complex was tested in Mueller–Hinton (MH) agar plates. The microorganisms (*E. coli*, *P. aeruginosa*, and *S. aureus*) were transferred to separate test tubes containing 5.0 mL of sterile brain heart infusion (BHI) medium and incubated for 18 h at 35–37°C. Sufficient inocula were added in new tubes until the turbidity equaled 0.5 McFarland ($\sim 10^8$ CFU mL^{-1}). The bacterial inocula diluted with BHI (McFarland standard) were uniformly spread using sterile cotton swabs on sterile Petri dishes MH agar.

Sterile filter paper discs of 10 mm in diameter were aseptically impregnated with 330 μg of the Au(I)–NAC complex according to the following procedure: a suspension of 16.6 mg of Au(I)–NAC in 1000 μL of DMSO was homogenized in a vortex and 20.0 μL of the suspension was collected using a micropipette and transferred to the paper discs. Sterile discs impregnated with 660 μg of pure NAC and DMSO were used as a negative control. Discs impregnated with NAC were prepared as follows: 16.6 mg of pure NAC were dissolved in 500 μL of water and 20 μL of the solution was transferred to the paper discs. Discs impregnated with Au(I)–NAC, DMSO, and pure NAC were dried and sterilized in a vertical laminar flow under UV radiation for 45 min before the experiment. All impregnated discs were placed on the surface of the solid agar. The plates were incubated for 18 h at 35–37°C and examined thereafter. Clear zones of inhibition formed around the discs were measured and the complex sensitivity was assayed from the diameter of the clear inhibition zones (in millimeter). Experiments were performed in triplicates.

3. Results and discussion

3.1. *SSNMR spectroscopy*

The structural formula of NAC with hydrogen and carbon numbering is shown in figure 1.

Solution ^{1}H- and ^{13}C–{^{1}H}-NMR spectra of the Au(I)–NAC complex could not be obtained due to the insolubility of Au(I)–NAC in water and other common organic solvents. So, the CP–MAS SSNMR technique was applied to assign the ^{13}C peak positions [24, 25]. The NMR spectrum of Au(I)–NAC was analyzed in comparison to the spectrum of free NAC. The ^{13}C-NMR spectra are shown in figure 2.

The sulfur coordination of NAC to Au(I) is attested by analyzing the ^{13}C-NMR spectra. The chemical shift for C_3 (bonded to sulfur) in the spectrum of the free ligand is at 28.6 ppm, while in the spectrum of the complex, it is at 37.1 ppm ($\Delta\delta$ of 8.5 ppm). For the palladium(II) and platinum(II) complexes with NAC [20, 21], sulfur

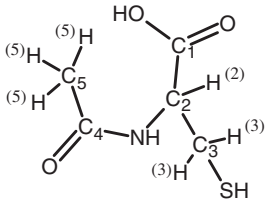

Figure 1. Structural formula of NAC showing hydrogen and carbon numbering.

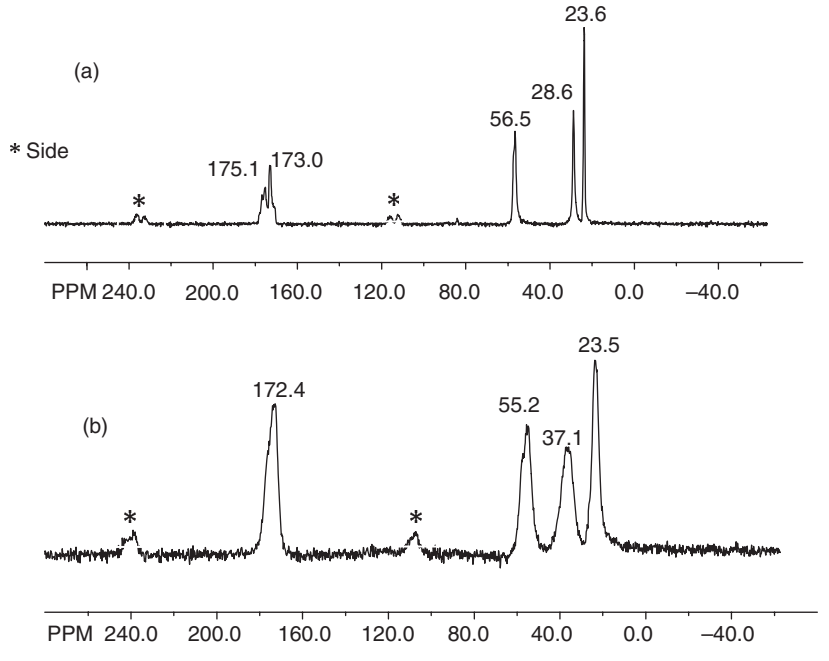

Figure 2. SSNMR spectra of NAC (a) and Au(I)–NAC (b).

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coordination to Pd(II) and Pt(II) was proposed based on a coordination shift in the range 6.0–6.5 ppm. Moreover, in the case of metal complexes with glutathione, peaks attributed to carbon near the thiol group appeared to be affected most by sulfur coordination [26]. The ^{13}C-SSNMR chemical shifts for NAC and Au(I)–NAC are summarized in table 1. Broadening of ^{13}C-NMR signals in the complex spectrum may arise from the presence of two energetically similar conformers in the solid state (polymorphism). Also, the presence of more effective intermolecular interactions in the solid state can result in the broadening of ^{13}C-NMR signals [27, 28].

Possible nitrogen and oxygen coordination to Au(I) were also studied by comparing the SSNMR spectra of the free ligand and the Au(I)–NAC complex. The chemical shift for C_2, bonded to nitrogen, is at 56.5 ppm in the ligand, while for the complex, it shifts upfield to 55.2 ppm ($\Delta\delta$ of 1.30 ppm). This minor change suggests that nitrogen is not coordinated to Au(I). For the Pt(II) complex with 3-hydroxypicolinic acid, nitrogen–platinum coordination produces shifts of the carbon bonded to nitrogen of 3.8–5.0 ppm (solution-state ^{13}C-NMR) [29]. The non-coordination of NAC to Au(I) through nitrogen is reinforced by considering IR data (section 3.2).

Chemical shifts of 175.1 and 173.0 ppm in the spectrum of NAC are assigned to the carbons of the carboxyl and acetyl groups (C_1 and C_4 in figure 1), respectively. In the spectrum of the complex, the chemical shifts for C_1 and C_4 appear at 172.4 ppm. Although minor chemical shifts ($\Delta\delta$ of 2.80 ppm) were observed for C_1 in the spectrum of the complex when compared to the ligand, the presence of a well-defined absorption band at 1726 cm^{-1} in the IR spectrum of complex (section 3.2) clearly indicates that the carboxylic group remains protonated and uncoordinated. Moreover, the minor chemical shift of 0.60 ppm for C_4 when ligand and complex ^{13}C-NMR spectra are compared also indicates that neither nitrogen nor oxygen of the amide group of NAC is coordinated to Au(I). Similar results were observed for the Pt(II)–NAC complex, recently published [21].

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3.2. *IR spectroscopic measurements*

The Au(I)–NAC IR spectrum was analyzed in comparison to the IR spectrum of free NAC. The IR spectra of NAC and Au(I)–NAC are provided in the "Supplementary material".

The IR spectrum of NAC exhibits a strong absorption band at 1718 cm^{-1}, which is assigned to the un-ionized carboxylic group [30]. The presence of the same band at 1726 cm^{-1} in Au(I)–NAC complex spectrum is an evidence that the carboxylic group remains non-coordinated as proposed by ^{13}C-NMR analysis.

The IR spectrum of NAC shows a sharp absorption band at 2548 cm^{-1}, which is attributed to the S–H stretching absorption band. The absence of this band in the

Table 1. ^{13}C chemical shifts for NAC and Au(I)–NAC.

	Chemical shifts (ppm)				
Compounds	C1	C2	C3	C4	C5
NAC	175.1	56.5	28.6	173.0	23.6
Au(I)–NAC	172.4	55.2	37.1	172.4	23.5

Au(I)–NAC spectrum suggests that the SH group lost its hydrogen, being coordinated to Au(I) [30, 31].

The possible nitrogen coordination of NAC to Au(I) was also considered by comparing the N–H absorption in the IR spectra of NAC and the complex [30, 32]. According to the literature, if coordination occurs through nitrogen, the hydrogen of N–H is most likely lost and the N–H vibration would disappear from the IR spectrum of the complex [19, 33]. The N–H vibration mode in the spectrum of the ligand is observed as a sharp band at 3375 cm^{-1}, while in the spectrum of the complex, the N–H vibration is assigned to the broad band with a maximum at 3296 cm^{-1}; the presence of the N–H absorption band in the IR spectrum of the complex further supports the non-coordination of NAC to Au(I) through nitrogen as proposed by NMR data. As previously described for Pt(II)–NAC complex [21], broadening of the N–H band in the spectrum of Au(I)–NAC is likely due to the presence of water molecules, which form hydrogen bonds in the solid complex [30].

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3.3. *Thermal analysis*

Thermogravimetric (TGA) curve for the Au(I)–NAC complex is provided in the "Supplementary material". According to the thermogravimetric data, the hydrated water is lost at the beginning of heating at temperatures not exceeding 100°C. Anal. Calcd for the loss of 0.75 H_2O molecule (%): 3.62. Found (%): 3.31. The oxidation of the ligand starts near 180°C, leading to the formation of Au^0 at 700°C.

The DTA curve for the Au(I)–NAC complex exhibits exothermic peaks with maxima at 341°C, 435°C, and 550°C. These effects are assigned to ligand oxidation in three steps, leading to the formation of Au^0 as the final residue.

3.4. *Biological activity*

Antibiotic sensitivity profiles of bacterial strains demonstrate the antibacterial activity of the Au(I)–NAC complex against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) microorganisms, as observed by the disc diffusion method. Impregnated filter discs with the Au(I)–NAC complex exhibit inhibition zones for *E. coli*, *P. aeruginosa*, and *S. aureus* of 16.00 ± 0.05 mm, 14.00 ± 0.05 mm (diffuse inhibition zone), and 18.00 ± 0.05 mm, respectively. The inhibition zone of 16.00 ± 0.05 mm for *E. coli* indicates that this bacterial strain is sensitive to the Au(I)–NAC complex, being comparable to standard antibiotics, Gentamycin and Tetracycline [23]. For *S. aureus*, the inhibition zone of 18.00 ± 0.05 mm also indicates the sensitivity of this bacterial strain to Au(I)–NAC complex, being comparable to standard drug oxacilin [23].

The observed activity of Au(I)–NAC complex against a Gram-positive microorganism is similar to the antimicrobial behavior of phosphine–gold(I) complexes with 2-mercaptopropionic and 6-mercaptonicotinic acids (showing S-coordination) and also with gold(I) complexes with imidazole and pyrazole [10, 34]. In the case of *P. aeruginosa*, the presence of a diffuse inhibition zone after incubation for 18 h led us to consider the resistance of this bacterial strain to the Au(I)–NAC complex in the tested concentration.

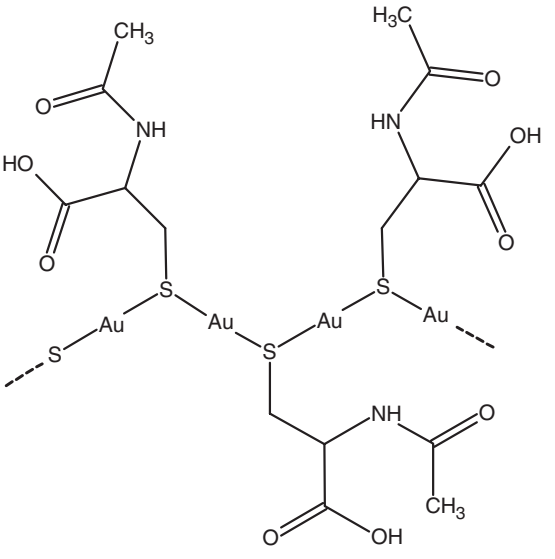

Figure 3. Structural formula proposed for Au(I)–NAC. Water hydration was omitted.

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Pure NAC was also submitted to antibiogram assays against the same bacterial strains, but did not exhibit antibacterial activity against *E. coli*, *P. aeruginosa*, or *S. aureus* in the same experimental conditions.

4. Conclusions

The molar composition of the Au(I)–NAC complex was 1 : 1 (metal : ligand). Water content was confirmed by thermogravimetric analysis. SSNMR and IR data support coordination of the ligand to Au(I) *via* sulfur. Based on the chemical and spectroscopic results, a schematic structure for the Au(I)–NAC complex is shown in figure 3. The suggestion of a polymeric structure is supported by the previously published results on $[Pt_2(\mu\text{-NAC-S})_2(bpy)_2]$ (bpy = bipyridine) and $[(NAC\text{-}S)(H_2O)Pt(\mu\text{-}NAC\text{-}S)_2Pt(H_2O)(NAC\text{-}S)] \cdot H_2O$ where the sulfur of NAC bridges two metals [19, 21]. The insolubility of the complex in both polar and non-polar solvents reinforces the proposition of the polymeric structure, as observed for other polymeric metal complexes involving α-amino acids [35–37].

Biological studies revealed the antibacterial activity of the complex against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) microorganisms.

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